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Polymeric surfactants for enhanced oil recovery: A review



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ABSTRACT

Chemical enhanced oil recovery (EOR) is surely a topic of interest, as conventional oil resources become more scarce and the necessity of exploiting heavy and unconventional oils increases. EOR methods based on polymer flooding, surfactant-polymer flooding and alkali-surfactant-polymer flooding are well established, but new challenges always emerge, which give impulse to the search for new solutions. Polymeric surfactants represent a very attractive alternative to these techniques, because they can provide simultaneously increase in water viscosity and decrease in interfacial tension, both beneficial for the efficiency of the process. The analysis of the literature shows that the use of polymeric surfactants as displacing fluid has the potential to improve the performances of EOR in some cases. However, the synthesis are often challenging and costly and the available data about the real performances of such systems in oil recovery are still sparse. This holds back the possibility of a significant use of polymeric surfactants for EOR. This review collects the relevant work done in the last decades in developing and testing polymeric surfactants for EOR, with a particular emphasis on the chemical aspects, the patent literature and bio-based systems.

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1. Introduction

Chemical methods for enhanced oil recovery (EOR) consist of the injection of a displacing fluid in oil reservoirs to mobilize the crude oil trapped in the porous rocks. The displacing fluid generally is a water solution containing various additives. Typically,

the mixture contains a water soluble polymer (this technique usually is referred to as polymer flooding), alone or in combination with a surfactant (surfactant-polymer flooding, or simply SP flooding) and/or an inorganic base (alkali-surfactant-polymer flooding, ASP). All these techniques have been extensively described in books and review articles (Lake, 1989; Green and Willhite, 1998; Thomas, 2008; Alvarado and Manrique, 2010; Sheng, 2010; Nazar et al., 2011; Olajire, 2014).

The polymer is used to increase the viscosity of the water, while the surfactant acts as emulsifier. The scope of the base (generally a hydroxide such as NaOH or a carbonate) is essentially the same as the surfactant: the base reacts with the organic acid components contained in acidic crude oils, forming surfactants in situ (Thomas, 2008). Also, besides generating the surfactants, alkali are added to reduce the adsorption of anionic surfactants on certain rock

Abbreviations: AA, acrylic acid; AM, acryl amide; ASP, alkali-polymer-surfactant flooding; BA, butyl acrylate; Ca, capillary number; DLS, dynamic light scattering; EA, ethyl acetate; EOR, enhanced oil recovery; HMPAM, hydrophobically modified poly(acryl amide); HPAM, partially hydrolized poly(acryl amide); IFT, interfacial tension; M, mobility ratio; PAM, poly(acryl amide); PEO/PEG, poly(ethylene oxide); PPO, poly(propylene oxide); PVA, poly(vinyl alcohol); SP, polymer-surfactant flooding; VA, vinyl acetate

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matrix. Many studies discuss about the issue of anionic surfactants adsorption on positively charged clay edges in sandstones and positively charged matrix in carbonate surfaces at neutral pH. This issue is not treated in detail in this review, but the interest reader can refer to other more specific reviews on the topic (Olajire, 2014; Hirasaki et al., 2011).

The mechanism of enhanced recovery involved in polymer flooding is based on decreasing the mobility difference between displacing and displaced fluids, in order to reduce fingering effects. The displacing phase should have mobility equal to or lower than the mobility of the oil phase (Ezell and McCormick 2007; Rashidi et al., 2010). When the water/oil mobility ratio (M) is 1 or slightly less, the displacement of the oil by the water phase will occur in a piston-like fashion. By contrast, if M is greater than 1, the more mobile water phase will finger through the oil, causing a breakthrough and poor recovery. Since the mobility is inversely proportional to the viscosity, the polymer should act as an effective viscosifier for the aqueous phase. The main features of such polymers are: very high molecular weight, resistance to mechanical degradation in shear and, of course, complete solubility in water. Additionally, they should be inexpensive, non-toxic and able to tolerate high salinity and high temperatures. The polymeric systems traditionally employed for EOR have been extensively reviewed recently (Wever et al., 2011).

In surfactant flooding, the recovery mechanism is based on lowering the interfacial tension between the two phases (IFT). The role of IFT in oil recovery is better explained in terms of capillary number (Ca), as discussed in more detail in the next section of this review. The state of the art of surfactant flooding has been reviewed recently (Hirasaki et al., 2011).

In EOR processes which combines the two mentioned mechanisms, (SP or ASP flooding), some factors should be considered, such as interactions between polymer and surfactant, loss of surfactant through solubilization in the oil phase or adsorption on the rocks and chromatographic separations of the various components, which could be detrimental for the whole process (Sheng, 2010).

For these reasons, the possibility to combine the positive effects of polymers and surfactants in only one component, namely a polymeric surfactant, becomes an attractive alternative for the traditional EOR processes. Indeed, the potential of polymeric surfactants for EOR has been often claimed (Ezell and McCormick, 2007; Winnik and Yekta, 1997; Shaikh et al., 1999; Crevecoeur et al., 1999; Al-Sabagh, 2000; McCormick et al., 2006; Busse et al., 2002; Desbrieres and Babak, 2010; Sun et al., 2010; Elraies et al., 2011; Fischer et al., 2001; Raffa et al., 2015).

It is very interesting to note that, in a way, polymeric surfactants have been used since long time in EOR, without really recognizing them as such. The idea of introducing hydrophobic groups in a water-soluble polymer, which actually makes it a polymeric surfactant (see next section), has been applied in EOR (Wever et al., 2011; Taylor and Nasr-El-Din, 1998). Several structures based on hydrophobically modified polyacrylamide (HMPAM) or polysaccharides have been proposed and even patented (Wever et al., 2011; Taylor and Nasr-El-Din, 1998). However, the hydrophobic groups are introduced mainly to alter the rheology of the system: it has been observed that the hydrophobic domain can form shear-dependent transient association in water with subsequent solution thickening (Winnik and Yekta, 1997; Taylor and Nasr-El-Din, 1998; Kudaibergenov and Ciferri, 2007). The focus is usually on the effect of hydrophobic interactions (Wever et al., 2012, 2013a, 2014) or of the chemical structure (Wever et al., 2013b, 2013c, 2013d) on the rheology, while a study of the surface properties is usually neglected. Actually, the presence of hydrophobic parts in water-soluble structures is also known to affect the interfacial properties (surface tension, IFT,

wettability). Therefore, even if for polymeric surfactants the effect is usually less pronounced than for low-molecular weight surfactants (Raffa et al., 2015), this aspect should be considered when hydrophobically-modified polymers are investigated as potential systems for EOR.

Very general and complete reviews about EOR and traditional polymeric systems used for this application can be found elsewhere (Lake 1989; Green and Willhite, 1998; Thomas, 2008; Alvarado and Manrique, 2010; Sheng, 2010; Nazar et al., 2011; Wever et al., 2011; Taylor and Nasr-El-Din, 1998). Here, we will consider polymeric surfactants that have been proposed for EOR, especially from the point of view of their interfacial properties. First, the relevant properties of polymeric surfactants for EOR will be discussed, then the available literature on the systems proposed, both in the open and in the patent literature will be presented.

In the conclusions and outlook section, the current issues, perspectives and some general criteria for the selection of potential new candidates to be employed as polymeric surfactants for EOR will be given.

2. Requirements of polymeric surfactants for EOR

Polymeric surfactants are macromolecules which contain both hydrophilic and hydrophobic parts in their structure. Compared to traditional surfactants, the macromolecular nature of these systems allows a much larger variety of structures. For example, a polymeric surfactant can simply be derived by the polymerization of a surface-active monomer (in this case they are usually known as polysoaps) or by the copolymerization of an hydrophobic and a hydrophilic monomer. In this latter case, the distribution of monomers can be varied. This kind of copolymers can thus have a random, a gradient, or a block structure. Amphiphilic diblock copolymers are basically the macromolecular transposition of low-molecular weight surfactants and, consequently, they are commonly referred to as “macrosurfactants” (Raffa et al., 2015). Moreover, not only linear structures are possible, but also polymeric surfactants with more complex architecture can be made (graft, star, dendrimers, etc.).

Polymeric surfactants usually present very interesting rheological and interfacial properties (Raffa et al., 2015). Logically, most of these properties will derive from their chemical structure. For example, polysoaps are known to have good emulsification properties, but poor solution viscosity, while macrosurfactants, especially the ones containing a polyelectrolyte block, present excellent gelation properties but low surface activity (Raffa et al., 2013, 2014). Without discussing the details, these characteristic derive mostly from the mechanisms of aggregation in solution. The chemical composition is also very important in determining the final properties. A very important feature of some polymeric surfactants is the possibility to tune their hydrophobicity, and thus their aggregation behavior, by changing external parameters, such as pH, temperature or electrolytes concentration. These kinds of polymers are important building blocks for smart materials. Of course, depending on the application that one has in mind, some structures will be more suitable than others.

For all these reasons, polymeric surfactants attracted a lot of interest for actual or potential applications in several fields including (mini)emulsion polymerizations, coatings, biotechnology, medicine, pharmacology, cosmetics, agriculture, water purification, electronic, optoelectronic and enhanced oil recovery (Winnik and Yekta, 1997; Kudaibergenov and Ciferri, 2007; Kwon and Kataoka, 1995; Alexandridis, 1996; Torchilin, 2001; Adams et al., 2003; Popot et al., 2003; Gil and Hudson, 2004; Taubert et al., 2004; Rodriguez-Hernandez et al., 2005; Garnier et al., 2006; Kudaibergenov et al., 2006; Dai et al., 2008; York et al., 2008;

Blanazs et al., 2009; Jiang et al., 2009; Zhou et al., 2009; Zhou and Yan, 2009; Tadros, 2009; Durand and Marie, 2009; Cayre et al., 2011).

The importance of solution rheology for EOR is mostly connected to the need of adjusting the mobility ratio by increasing the water phase viscosity, as it has been already emphasized in the introduction. This applies in a general way for polymer flooding. In surfactant flooding, the displacing water solution needs to be able to create a stable emulsion with the oil in flow conditions. Theoretically, it is well established that the process of emulsion formation in laminar flow is governed by the balance between the viscous force acting on a drop in a laminar flow field and the Laplace pressure (Walstra, 1993; Grace, 1982). The dimensionless ratio between the viscous-to-capillary forces is called Capillary number (Ca). This parameter has been related to the residual oil saturation in porous media and thus it is very important for EOR applications (Lake, 1989; Sheng, 2010). The capillary number can be defined for several purposes. For EOR it is convenient to base the calculation on the force balance on a drop of oil squeezed through a pore throat Reed and Healy (1977). In this case we have:

$$Ca = \frac{\nabla P \cdot k}{\gamma}$$

where ∇P is the gradient pressure, γ is the interfacial tension between the two immiscible phases (often also indicated with IFT) and k is a constant. According to Darcy's law the equation can be rewritten as:

$$Ca = \frac{v \cdot \eta_c}{\gamma}$$

where η_c is the viscosity of the continuous phase and v is the Darcy velocity. Other formulations of Ca have been proposed, which take into account parameters such as porosity, relative permeability and contact angle, but this form is the most used because of its simplicity.

Typical Ca in waterflooding are in the order of magnitude of 10^{-8} – 10^{-7} . It is generally assumed that for a substantial increase in oil productions the Ca values should be increased by at least 2–3 orders of magnitude, meaning that surfactants should be able to give low to ultralow values of γ ($\gamma \leq 10^{-1}$ mN/m) (Green and Willhite, 1998; Iglaue et al., 2010; Abrams, 1975).

The use of polymeric surfactants could represents a favorable option since in principle a decrease in interfacial tension and an increase in viscosity are expected to occur at the same time, with a subsequent positive effect on Ca . Moreover, being a polymeric surfactant a single component and not a mixture, this approach should also have the advantage of avoiding the segregation into two phases that can occur in a flow stream for conventional polymer-surfactant mixtures (Sheng, 2010; Nazar et al., 2011; El-raies et al., 2011).

The choice of a suitable system on the basis of the above considerations is not trivial. For example, several polymeric surfactants show very low or even negligible surface activity (Jacquin et al., 2010; Theodoly et al., 2009; Jacquin et al., 2007; Ghosh et al., 2011; Nayak et al., 2011; Kaewsaiha et al., 2005; Matsuoka et al., 2004). This lack of surface activity is usually explained with a very slow equilibration of polymeric surfactant micelles (the so-called “frozen” micelles (Theodoly et al., 2009)), which prevent the possibility of the macromolecules to migrate to the interfaces. As clearly documented in literature (Raffa et al., 2015), the structure and the composition of amphiphilic polymers are fundamental to determine surface properties and rheology of their aqueous solutions. Also, the physical properties and behavior can be greatly affected by pH, temperature, presence of dissolved salts and kind of flow.

Other hardly quantifiable characteristics that a suitable polymeric surfactant should possess, are the same as for traditional polymers for EOR: low adsorption on the rocks, high thermal stability and salt tolerance.

3. Polymeric surfactants for EOR

The idea to use polymeric surfactant for EOR, which can in principle act either as solution thickeners and surfactants, is not new. Indeed, most of the systems successfully employed or proposed as solution thickeners based on hydrophobically modified water soluble polymers (recently very extensively reviewed¹¹) can in principle also act as surfactants, although the surface activity of such systems usually is not considered in the studies (see introduction). In order to improve interfacial activity and ability of polymer to solubilize and emulsify crude oil, the surfactant-containing mixtures, such as SP or ASP flooding systems were developed. However, due to the different properties, such mixtures often separate into two phases in a flow stream. Other problems can be attributed to the attraction of surfactant to rock-water interface, which can result in the loss of surfactant to reservoir rock surface by adsorption (Yu et al., 2008), or to the incompatibility between surfactant and polymer, resulting in the decline of polymer properties, such as aggregation, adsorption, and diffusion performance in porous media (Sun et al., 2010). Moreover, in cases where ASP flooding has proven to successfully increase oil recovery in the field, the presence of the strong alkali has detrimental effects on polymer performance. In many cases additional polymer is required to achieve the desired viscosity (Elraies et al., 2011), although it is believed that the alkali positively affects the process, as briefly discussed in the introduction.

A polymeric surfactant that combines the high viscosity of a polymer with the interfacial property of a conventional surfactant could reduce the tension at water/oil interfaces and enhance the viscosity of the aqueous solution simultaneously (Cao and Li, 2002).

Such an approach has already been applied in some fields but, because it is often observed that polymeric surfactants have only a slight ability to decrease the IFT, relatively few use of polymeric surfactants in EOR have been reported. However, the common belief that ultralow IFT (order of magnitude of 10^{-3} mN/m) values are needed for good performance in EOR has been recently questioned. Zhang et al., (2010) Some recent SP flooding experiments (Yu et al., 2010) showed that in some cases there is not a straightforward correlation between lowering the IFT and recovery, but there is rather an optimum IFT, which is higher than the stated ultralow values (Fig. 1). The claim that ultralow IFT values are not strictly necessary to improve oil recovery seems to be supported also by a very recent study, dealing with a polymeric surfactant rather than a SP mixture: here, a surface active modified HPAM solution with a measured IFT of 10^{-1} mN/m, gives ~5% more oil recovery than a conventional HPAM in a core-flood experiment, at even lower viscosity (Co et al., 2015).

Several papers (Shaikh et al., 1999; Crevecoeur et al., 1999; McCormick et al., 2006; Busse et al., 2002; Fischer et al., 2001; Theodoly et al., 2009; Qin et al., 1994; Iddon et al., 2004; Yahaya et al., 2001; Kudaibergenov, 1999; Dimitrov et al., 2007; Jain and Bates, 2003; Hietala et al., 2007; Zaroslov et al., 2005; Liu et al., 2007; de la Fuente et al., 2005) published in scientific journal propose various amphiphilic polymers as systems for EOR. Despite this, only few studies cover experiments performed to prove the effectiveness of such systems for the claimed application. We could identify few papers in which viscosity, surface properties and salt effects are taken into account for the evaluation of a given polymeric surfactant in EOR performance.

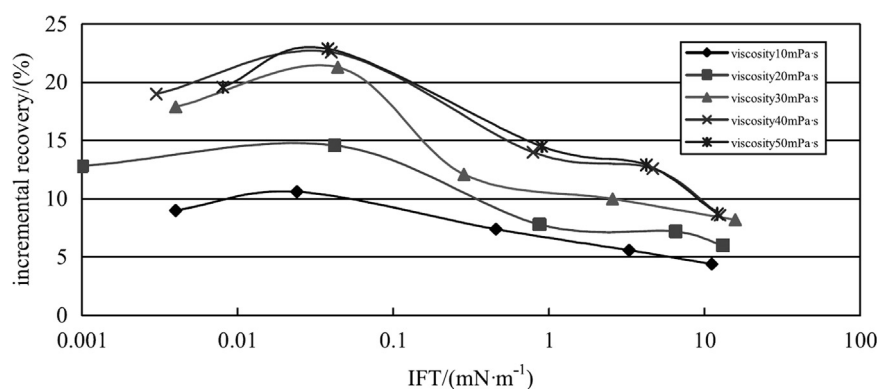


Fig. 1. Relationship between incremental recovery and IFT in SP flooding experiments. Reprinted with permission from Ref. (Yu et al., 2010).

In one of the first published studies on EOR concerning simultaneously optimization of rheological properties and interfacial behavior of amphiphilic polymers, alternating copolymers of alkenes and maleic anhydride were prepared by free radical polymerization and hydrolyzed to obtain an anionic polysoap (Yahya and Hamad 1995).

Surface and interfacial activities (water vs *n*-decane) are good (45.0 and 8.68 mN/m respectively) and IFT decreases in the presence of salt (1.05 mN/m at 1 wt% NaCl concentration; at higher salt concentration, a salting-out effect is present). However, the viscosity of the solutions is moderate even at high polymer concentrations, because intramolecular aggregations are predominant, as usually happens for polysoaps. When 1-hexadecene is used as co-monomer, results in terms of both viscosity and interfacial activity are better compared to 1-dodecene, due to the increased hydrophobicity. An analogous increase in interfacial activity upon addition of NaCl was observed for a viscosifier based on hydrophobically modified PVA (Yahya et al., 1996). Also in this case, an optimization study to maximize both surface activity and viscosity has been performed.

Good viscosifying properties and surface tension reduction have been obtained with amphiphilic block copolymers based on Polystyrene-*b*-poly(sodium methacrylate), containing a PEG-acrylate comonomer in the hydrophilic block, synthesized by ATRP (Raffa et al., 2016). The presence of the charged sodium acrylate is necessary to achieve high viscosity, while the PEG moiety ensures the lowered surface tension. In presence of NaCl, the viscosity decreases due to electrostatic interactions, but a better surface activity is also measured.

As anticipated, even if their surface and interface properties received little or no attention, hydrophobically modified water

soluble polymers, extensively used as solution thickeners in EOR, can also act as polymeric surfactants. For example, the introduction of 1% of hydrophobic acrylates in a polyacrylamide strongly increases the stability of water/oil emulsions (Fig. 2) (Zhao et al., 2009).

An analogous polymer is capable of stabilizing water/*n*-heptane and water/oil mixtures, even in the presence of NaCl and NaOH in a simulation of ASP flooding formulation (Sun et al., 2010).

PAM containing 2–3 wt% *N*-phenethylacrylamide units distributed in a blocky way shows a decrease of surface tension as well as a decrease in interfacial tension between water and *n*-decane. Interestingly, the polymer containing the lowest number of hydrophobic groups is more effective in reducing the surface tension, but is less effective in decreasing the interfacial tension. This has been explained by the authors with the consideration that for higher numbers of hydrophobic groups, the polymer's ability to form intramolecular aggregates increases as well, determining a major stabilization in solution and consequently a minor adsorption at the interface. The reverse behavior in IFT measurements has been explained by the good solubilization ability of the hydrophobe by *n*-decane, which provides the hydrophobes with a more favored environment than the air phase and the hydrophobic aggregates. As a result, the hydrophobes adsorb at the interface as much as they can in the absence of competition by hydrophobic aggregation. Self-aggregation also helps to explain the reduced surface activity at high polymer concentrations (Abu-Sharkh et al., 2001).

The nature of the hydrophobic groups seems to play a crucial role in interfacial activity. Multi-block (with a random distribution of blocks) copolymer of acrylamide (AM) with styrene (Shaikh et al., 1999), phenylAM (Abu-Sharkh et al., 2003) and benzylAM

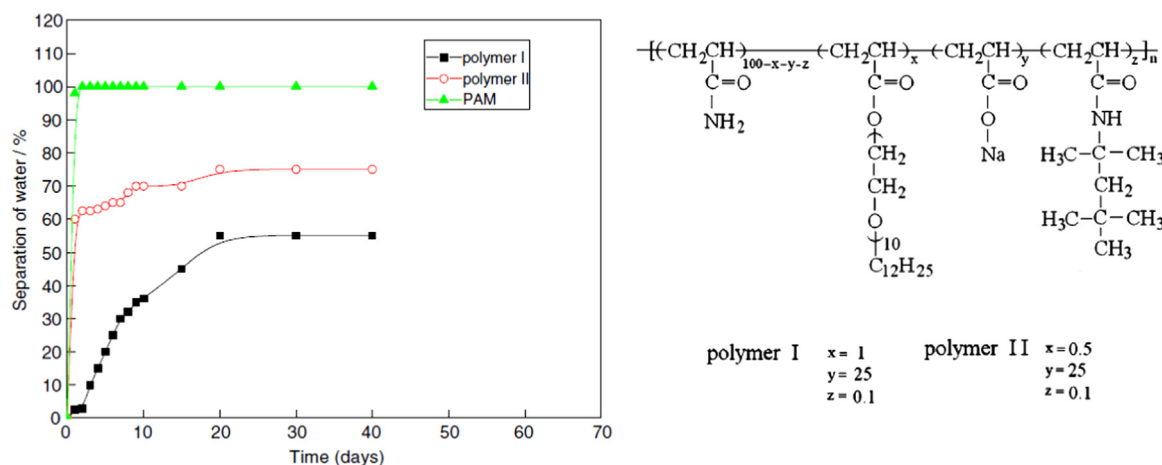


Fig. 2. Emulsion stability of water/oil mixtures with added hydrophobically modified PAM. Adapted with permission from Ref. (Zhao et al., 2009).

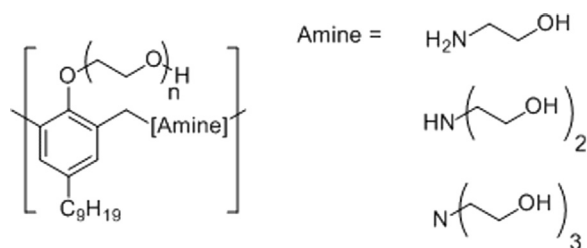


Fig. 3. Structure of the polymer studied in Ref. (Al-Sabagh et al., 2003) (redrawn with permission).

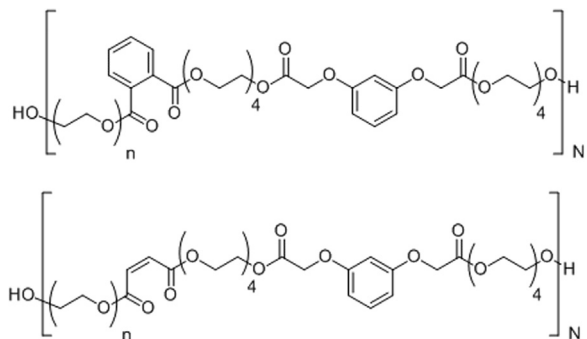


Fig. 4. Structure of the polymer studied in Ref. Al-Sabagh (2000) (redrawn with permission).

(Yahaya et al., 2001) showed different surface behavior. Apparently, the higher is the conformational freedom of the monomer (PhenethylAM > benzylAM > phenylAM > sty), the lower is the interfacial activity (Abu-Sharkh et al., 2001). All these AM based

polymers showed interesting salt effects: viscosity and interfacial activity in presence of added NaCl are unaffected or in some cases improved. Their properties make these polymers of potential interest for oil recovery.

Amphiphilic phenol-amine-formaldehyde resins (Fig. 3) were evaluated as systems for oil reclamation from soil. Results with both asphaltenic and waxy crude oils show that the amount of reclaimed oil is related to the IFT (Al-Sabagh et al., 2003). However, these can be considered more as oligomeric surfactants (Mw = 1000–5000).

Oligomeric polyesters (structure depicted in Fig. 4) have been prepared and studied for applications in EOR, proving to be suitable systems because of the ultralow IFT values (Al-Sabagh 2000).

A direct evaluation of the performance of polymeric surfactants in enhanced oil recovery is rarely found in literature. Traditional HPAM and hydrophobically modified ones (HMPAM) have been compared in core flood experiments (Lai et al., 2013; Maia et al., 2009). However, in those experiments, the viscosity of the HMPAM solutions are higher than the HPAM ones, which makes impossible to determine if the lowered interfacial tension (not measured) due to the presence of hydrophobic groups plays a role in the improved recovery. The authors only observed that the modified polymers present a better resistance to salt and thermal degradation.

A more convincing evidence of the role played by the IFT of a polymeric surfactant in oil recovery comes from a very recent research (Co et al., 2015). The authors compared the performance in core-flood experiments of a traditional HPAM and a HPAM modified incorporating 1–5% of a “surfactant-like monomer” (chemical structure not specified). In this study it is shown a positive effect of the reduced IFT (10^{-1} mN/m) on the oil recovery, even if the

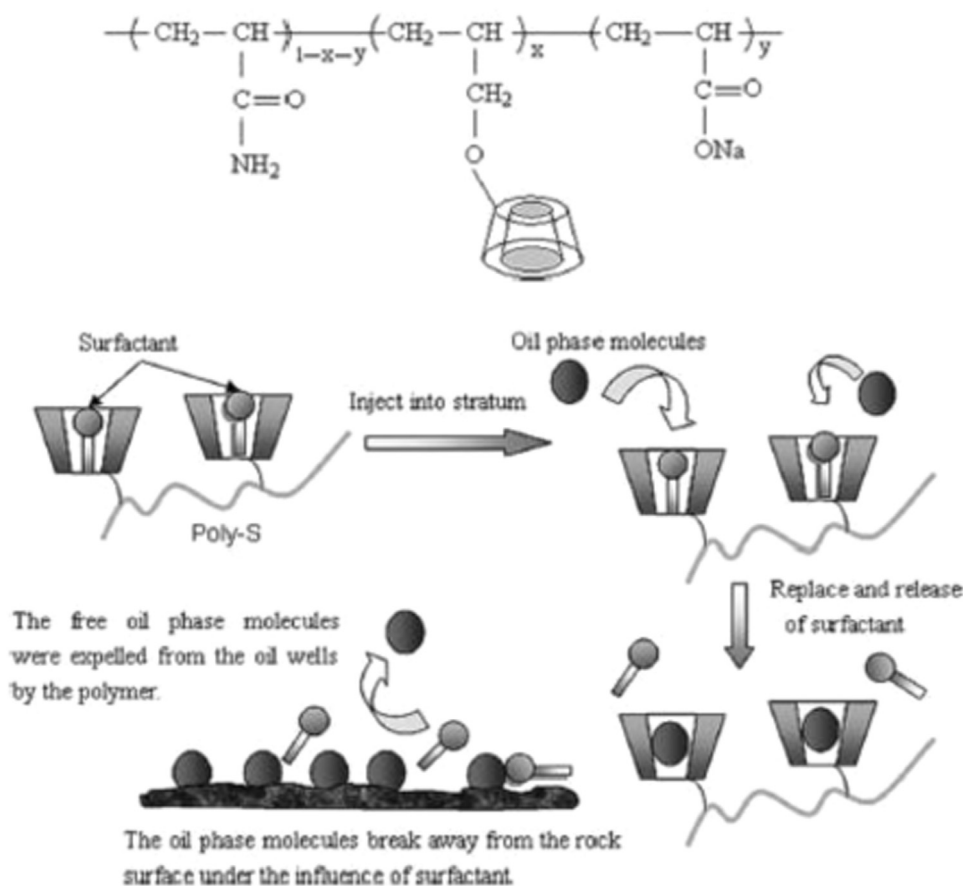


Fig. 5. Structure and proposed mechanism of action of cyclodextrin-substituted PAM. Adapted with permission from Ref. Zou et al. (2011).

polymeric surfactant solution in this case has lower viscosity and thus a less favorable mobility ratio than the HPAM.

An interesting concept has been proposed by Zou et al. They prepared a PAM containing cyclodextrin side groups (Fig. 5), claimed as a system for SP flooding. Their hypothesis is that the cyclodextrin side groups should form inclusion complexes with the surfactant molecules, preventing their loss during flooding experiments. Also, a synergistic effect has been suggested, since the oil phase can displace the surfactant in the hydrophobic cavity of the cyclodextrin, with subsequent “controlled” release of the surfactant molecules. Of course, the concept still needs to be proved and it seems to be hardly applicable from a practical point of view, also due to the high costs of cyclodextrin containing acrylic monomers.

3.1. Patents

Several patents concerning EOR and related applications of amphiphilic polymers have been deposited (van de Kraats and Sawyer, 1976; Byham et al., 1980; Chen and Sheppard, 1982, 1981; Evani, 1989; Huff et al., 2008, 2011; Savu and Sierakowski, 2010; Hough et al., 2010; Caneba, 2010; Favero and Gaillard, 2010; Zhang and Tang, 2010; Soane et al., 2011), focusing on their effects on both viscosity and interfacial tension between water and oil. A list is given in Table 1. Formulations can include the use of low molecular weight co-surfactants. For author's choice, oligomeric surfactants are not considered here.

A tapered copolymer of vinyl acetate (VA) and acrylic acid (AA) neutralized with ammonia has been patented (Caneba, 2010) as polymeric surfactant for EOR applications. Experiments of oil recovery with such tapered VA-AA (containing a certain amount of random copolymer) give a recovery of 17–41% OOIP. Hydrophobic acrylates (e.g. EA, BA) are proposed as substitutes of the VA, being more resistant to hydrolysis.

Alternate copolymers of styrene and secondary amines proved to be good viscosifier agents and showed pH-dependent emulsification ability, forming stable emulsions in basic conditions which separate as the pH is decreased (Soane et al., 2011).

A process for EOR recently patented, claims the use of a 25% hydrolyzed PAM modified with 0.4% of a cationic hydrophobic monomer. In this formulation, the polymer is used in combination with a very small amount of an anionic surfactant. It has been found that the emulsifying ability of this mixture is much better than the one of the surfactant alone, even at a surfactant concentration ten times higher (Favero and Gaillard 2010). The authors don't give any explanation for this behavior and define it “surprising”.

The polymer (Hough et al., 2010), a block copolymer of styrene, acrylic acid and ethyl acrylate (notably, prepared via controlled radical polymerizations), has been claimed as system for EOR. The viscosity of their aqueous solution is retained in the presence of high salt concentrations, provided that a non-ionic surfactant is included in the formulation.

Beside these specific examples, patents covering a very broad range of amphiphilic copolymers for EOR can be also found: a recent patent (Zhang and Tang, 2010) includes a broad range of partially hydrolyzed acrylamide based polymers, containing charged or neutral hydrophobic monomers, having IFT values included in the range 0.1–15 mN/m. Interestingly, the tested polymers give very good performance in terms of recovered oil in flooding experiments, proving to be much better than an analogous ordinary PAM with a higher viscosity.

The patent (Huff et al., 2008) by BASF includes a very general formulation for EOR consisting of a mixture of a surfactant and a polymeric co-surfactant. The co-surfactants are comb, multiblock or star copolymers build with hydrophobic units (essentially α -

olefins) and hydrophilic units (maleic anhydride, vinyl alcohol, (meth)acrylic acid, vinylpyrrolidone, allyl alcohol, PEO, PPO).

Surprisingly, most of the examples found in the patent literature are quite recent. Before 2008, the majority of patent literature concerning polymers for EOR includes mostly non-associative water soluble polymers.

3.2. Biobased systems

For evident reasons, polymers obtained by natural sources have also attracted attention as potential polymeric surfactants for EOR, looking for a cheap and green alternative to traditional systems. A sulfonated fatty ester surfactant, obtained by esterification and sulfonation of non-edible Jatropha oil (Elraies et al., 2010) has been free radically copolymerized with AM in order to synthesize a polymeric surfactant for EOR (Elraies et al., 2011). The structure of such polymer is not really defined, but is a cheap material, partly obtained from a renewable source, which possess good viscosity and interfacial activity, making it a good candidate for EOR.

Hydrophobically modified polysaccharides can show some surface activity and have been proposed for EOR applications (Desbrieres and Babak 2010). Their surface activities are generally low, because the usually rigid structures don't allow the rearrangement of the hydrophobic parts at water/air interface, as demonstrated, for example, for a pullulan hydrophobically modified fatty esters derivative 4–35% of substitution (Henni et al., 2005; Henni-Silhadi et al., 2008). The same observation has been made for chitin (Desbrieres and Babak, 2006) and pectin (Miralles-Houzelte et al., 2001) derivatives. In these latter cases, the surface properties seem to be better when the hydrophobic group is introduced as counter ion to the charged polysaccharide backbone, instead of covalently linked, while the rheological behavior is unaffected.

The surface and interface properties of a carboxymethylcellulose derived polymeric surfactant (Fig. 6) have been evaluated (Cao and Li 2002). As usually desired for EOR applications, the IFT reaches ultralow values (10^{-2} – 10^{-3} mN/m) in alkaline conditions, either with a sample of Daqing crude oil and with a mixture of alkanes. Interestingly, the IFT value is lowered in the presence of NaOH even for acid-free alkanes, which excludes the possibility of the formation of surfactants in situ by deprotonation of carboxylic acids that can possibly be already contained in the oil. The effect of decreasing the IFT is attributed to the disassembly of aggregates (as evidenced by DLS measurements), which allows rearrangement of the single polymer chains at the interface.

4. Conclusions and outlook

From a theoretical point of view, the use of polymeric surfactants for chemical enhanced oil recovery could represent a valid alternative to the commonly used systems, since they potentially combine desired rheological and interfacial properties in only one component, while in general mixtures of different chemicals are required. This would present the advantage to avoid separation and loss of some components during the flooding processes or unwanted interactions (Sheng, 2010). This potential is confirmed by the recent appearance in the patent literature of examples of polymeric surfactants for EOR (see Section 3.1). On the other hand, in most cases complex experimental procedures and expensive starting materials are required, which so far greatly limited this approach. In order to really exploit the potential of polymeric surfactants for EOR, the advantages should overcome the increased costs. Despite its academic interest, it is unlikely that the use of very expensive monomers in the formulation of polymeric surfactants for EOR (as the example in Ref. Zou et al. (2011)) would

Table 1

List of patented polymeric surfactants for EOR.

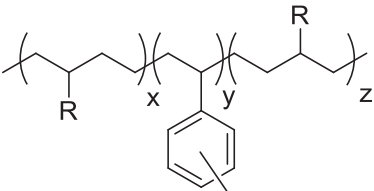
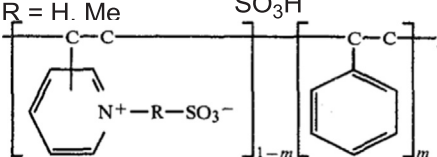
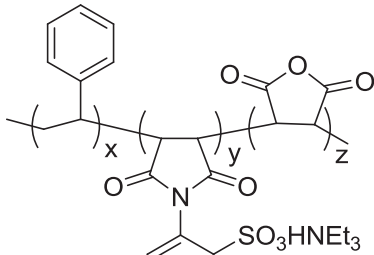
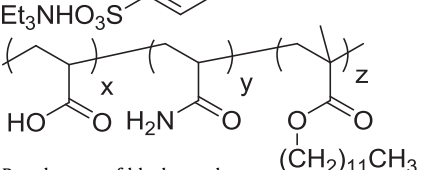
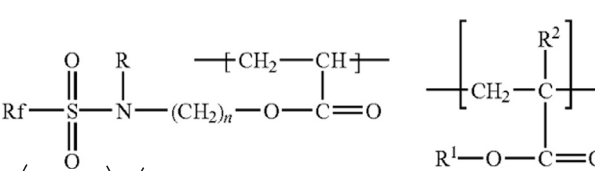
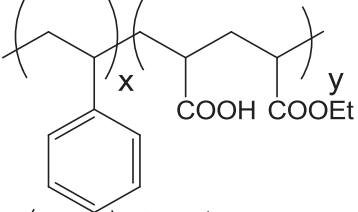
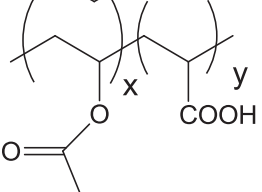
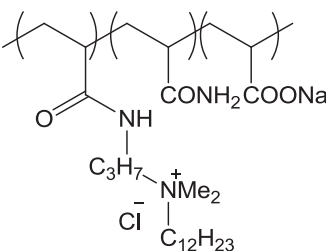
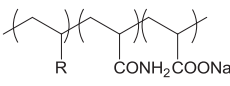
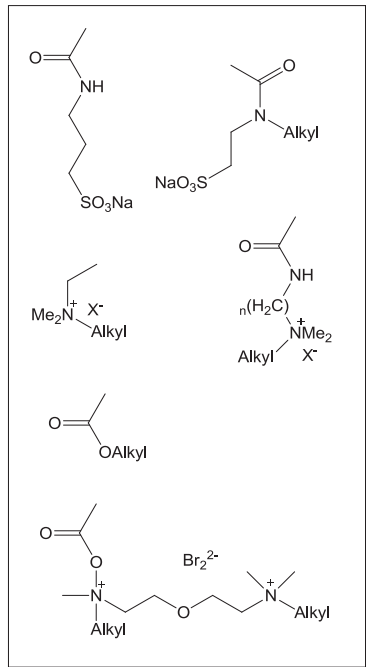
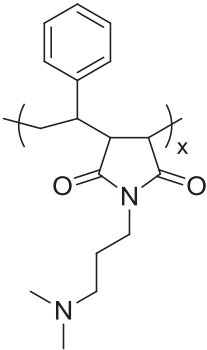
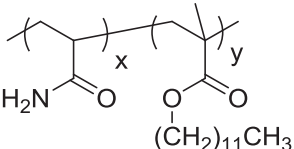
Ref	Chemical composition	Structure
(van de Kraats and Sawyer, 1976)		Triblock copolymer Mw hydrophilic = 100–2000 kDa Mw hydrophobic = 1–10 kDa
(Byham et al., 1980)	<p>R = H, Me</p> 	Diblock copolymer Mw > 50 kDa
(Chen and Sheppard, 1982, 1981)		1:1 Statistic copolymer 20–40% functionalized Mw = 3800 kDa
(Evani, 1989)		Multiblock Mw ~ 10 ³ kDa
(Huff et al., 2008, 2011)	Broad range of block copolymers	Comb, multiblock, star
(Savu and Sierakowski, 2010)		R _f = fluoroalkyl R ¹ = alkyl Random Mw > 100 kDa
(Hough et al., 2010)		Diblock 3 kDa (styrene) + 30 kDa (total acrylates)
(Caneba, 2010)		Tapered, ammonium salt
(Favero and Gaillard, 2010)		0.4% hydrophobically modified 25% hydrolyzed

Table 1 (continued)

Ref	Chemical composition	Structure
(Zhang and Tang, 2010)		<p>R =</p>  <p>statistic</p>
(Soane et al., 2011)		Alternate copolymer Mw=80 kDa
(Wilson et al., 2013)		<p>Multiblock Structure Micellar controlled polymerization 2 K < Mn < 25 K</p>

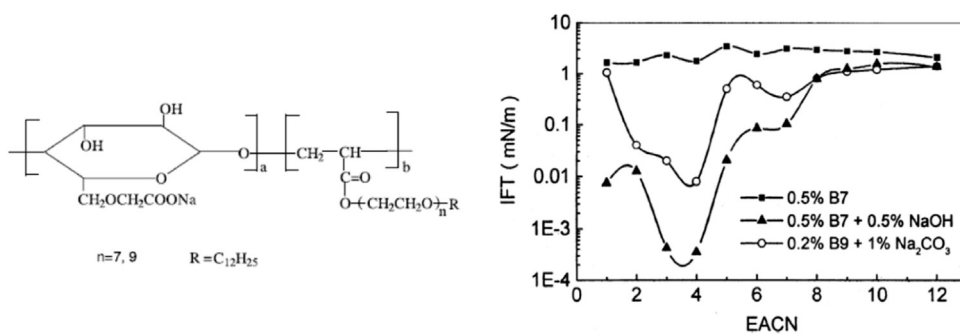


Fig. 6. Structure of the polymer studied in Ref. Cao and Li (2002) and IFT values as function of equivalent alkane carbon number (EACN). Adapted with permission.

represent a cost-effective option. In our opinion, a much more promising way is represented by the introduction of biopolymers and bio-based monomers (see Section 3.2). The clear advantages are constituted by availability of starting materials, sustainability and bio-compatibility. Again, the required chemical modifications and synthesis still limit this approach, but we believe that in would be worth to put some more effort in this direction.

The effectiveness of polymeric surfactants can be questioned on the basis of the fact that it is very difficult, if not impossible, to achieve ultralow values of IFT (for polymeric surfactants, typical values are found in the range 0.1–15 mN/m). This can be considered another aspect that holds back the use of polymeric surfactants for EOR. Ultralow IFT values have always been considered necessary in order to achieve sufficiently high values of capillary number and thus significant recovery (Lake, 1989). Nonetheless, this could be a too simplistic assumption, as recently shown by some experiments, where oil recovery using a SP formulation gave better results for intermediate values of IFT, rather than for ultralow ones (Yu et al., 2010). In our opinion, it can also be argued that measurements of surface and interfacial tension might not be the most appropriate to evaluate the effectiveness of a polymeric surfactant for EOR, because these parameters might become irrelevant in the time-scale of the process (it usually lasts for years).

Unfortunately, a clear picture cannot emerge yet, since not many experiments aimed at directly evaluating the performances of polymeric surfactants in oil recovery can be found in literature. Recently, core flood experiments performed with a traditional PAM and a hydrophobically substituted one, showed that the latter gives a better recovery than the former at the same polymer concentration (Lai et al., 2013). However, the systems are not compared at the same viscosity, so it is impossible to draw any conclusions regarding a possible role of IFT in the process. Actually, the authors of the mentioned work don't even consider the IFT as a relevant parameter, but they focus their discussion on salt tolerance and thermal stability.

As a general observation, and quite paradoxically, even though many hydrophobically substituted water soluble polymers (which are, at least in principle, polymeric surfactants) have been studied and even patented as solution thickeners for EOR, their interfacial properties have been rarely considered. Therefore, even if there are indications that they might perform better than non-hydrophobic polymers, it has not been clarified if - and to which extent - the interfacial behavior is important in determining the efficiency in oil recovery. Interestingly, it has been recently proposed, based on flooding experiments in an artificial porous medium, that even hydrolyzed PAM with no hydrophobic substitution could emulsify the oil during the flooding process (Meybodi et al., 2011).

Some issues still remain, that strongly limit the possibility of using polymeric surfactants in EOR. On one hand, the lack of clear indications that polymeric surfactants could really give better performances than traditional polymeric mixtures, other conditions being equal. Studies are still too sparse and not systematic, which makes any consistent investment in this direction too risky. Therefore, an important milestone is to produce more experimental data to establish if ultralow IFT values are really necessary in order to improve oil recovery. On the other hand, the costs of some of the starting materials can be very high and the complicated synthesis necessary to obtain polymeric surfactant not suitable for production in large scale. The scale-up might prove to be challenging especially for particular macromolecular architectures (such as block copolymers). In this respect, the most promising approach, also from the point of view of sustainability, seems to be the possibility to use monomers and materials from green feedstock. We think that more efforts in this directions are surely desirable.

To face the problems related to the decreasing oil availability,

more efforts from the scientific community and the exploration of economically suitable sources and processes are required.

In general, efforts in several directions are still required before polymeric surfactants can be really considered not only potential, but suitable systems for enhanced oil recovery.

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